ATTACHMENT 4

APPENDIX 2

TEST CHEMISTRY

INTRODUCTION

The Project Manager for Non-Stockpile Chemical Materiel is currently developing a mobile Rapid Response System for identification, segregation, repackaging, and/or treatment of recovered chemical agent identification set (CAIS). After the CAIS are unpacked in the unpack station of the glovebox, the contents of the bottles and ampules will be identified and the containers will be segregated accordingly. The CAIS components (ampules, bottles, and packaging material) that contain chemical agents will be chemically treated to form less toxic products as described by the processes discussed in this attachment. The CAIS components that contain industrial chemicals will be repackaged as lab packs in accordance with Department of Transportation regulations for safe handling and transportation from the RRS test site at Deseret Chemical Depot (DCD) to a hazardous waste treatment, storage, and disposal facility (TSDF). The following industrial chemicals will be repackaged in the RRS:

- Chloropicrin (PS) in chloroform, ampule;
- Phosgene (CG), ampule;
- Cyanogen chloride (CK), ampule;
- GA simulant [benzonitrile (2.6%), diethyl malonate (25.7%) heptanoic acid (2.3%), ethyl caprylate (17.8%), ethyl myristate (37.7%) ethyl heptanoate (2.0%), unidentified material (12.0%)], ampule;
- PS on charcoal, bottle;
- Chloroacetophenone (CN), bottle;
- Adamsite, (DM), bottle; and
- Triphosgene (CG simulant), bottle.

The chemical agents, sulfur mustards (HD and H), nitrogen mustards (HN-1 and HN-3), and lewisite (L), will be chemically treated in a 1 gallon reactor specially designed to handle the treatment of these substances. Throughout this permit application, treatment is the process of converting the chemical agents to products that do not exhibit the highly toxic properties of the chemical agent.

This attachment discusses the reactions for the treatment of HD and H [bis-(2-chloroethyl) sulfide], HN-1 [bis-(2-chloroethyl)ethylamine], HN-3 [tris(2-chloroethyl)-amine], and L [dichloro-(2-chlorovinyl) arsine] and the clean up of accidental spills in the RRS glove box. In this Permit, the term “treatment of chemical agents” refers only to the reduction or removal of particular toxic effects of the agent; other toxic effects may remain in the treated waste. Included in this attachment are the chemical properties of the chemical agents and the treatment reagents used in the chemical treatment processes. Reactions for the oxidation of HN-3 are similar to those for HN-1, they yield equivalent products, and they will not be discussed in this attachment.

Methods of handling these substances, and the hazards to personnel, are explained in Section D of the RRS Resource Conservation and Recovery Act Part B Permit Application. The methods of monitoring for exposure to these substances are also described in Attachment 4-8.

The six types of CAIS sets found in storage are classified into the following three groups that contain chemical agents:

- Toxic gas sets, K941 and K942 CAIS: contain bottles of ≤ 118 mL of sulfur mustard (HD or H).

- Identification sets, K951, K952, K953, and K954: contain ampules of agents and industrial chemicals. The chemical agents in these sets are HD or H, HN-1, and L diluted in chloroform, with ≤ 10 volume% agent in a total volume of ≤ 40 mL.

- Navy training and replacement sets, K955, X302, X547, X548, X550, and X551**:** contain bottles with ≤ 25 mL of chemical agent (HD or H, HN-1, HN-3, and L) adsorbed on 3 ounces by volume (90 cc) of charcoal.

Some of the above CAIS also contain industrial chemicals. See Attachment 4-1 for a complete description of all the CAIS.

Data on the physical and chemical properties have been obtained from multiple sources. They include:

- Army documents, such as:
  - U.S. Army Armament Research and Development Command, Chemical Systems Laboratory. "Literature Survey of Physical and Chemical Properties of Agents VX, GD, HD, and HL." ARCSL-CR-80051, APG, MD, 1980.

- Handbooks, such as:
  - S. Budavari, ed. The Merck Index, 11th Edition, Merck & Co., Inc., Rahway, NJ, 1989
  - J.A. Dean, ed., Lange's Handbook of Chemistry, 13th Edition, McGraw-Hill Book Co., NY, 1985
  - T.E. Daubert and R.P. Tanner, Physical and Thermodynamic Properties

of Pure Chemicals, Design Inst. Phys. Prop. Data, Amer. Inst. Chem. Eng., Vol. 2, Hemisphere Publishing Corp., NY, 1991
  - N.I. Sax and R.J. Lewis, Sr., eds., Hawley's Condensed Chemical Dictionary, 11th Edition, Van Nostrand Reinhold Co., NY 1987.
- Chemical catalogs, such as those from:
  - Aldrich Chemical Co., Milwaukee, WI, 1992
  - Fluka Chemie AG, Buch, Switzerland, 1993.
- Manufacturer's technical information, such as:
  - Lonza, Inc. Specialty Chemicals, "Dantoin® DCDMH," and "Dantoin® DMH", Fair Lawn, NJ, 1992
  - Occidental Corp., "Chloroform, Technical Grade," Data Sheet, Dallas, TX 1987.
- Material safety data sheets (MSDSs), such as:
  - Lonza, Inc. Specialty Chemicals, "MSDS, Dantoin® DCDMH," Fair Lawn, NJ, 3/16/1992
  - Mallinckrodt, Inc., "MSDS, Butyl Alcohol-tert.," Paris, KY, 1989.

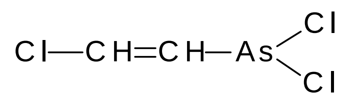
The data from these references were selected based on professional judgment. The MSDSs for the treatment reagents, solvents, and all of the substances expected in the CAIS will be available to the Rapid Response System operators and test personnel in the Rapid Response System Onsite Document Library. Copies are also included in Attachment 4-2.

CHEMICAL PROPERTIES OF CHEMICAL AGENTS FOUND IN CHEMICAL AGENT IDENTIFICATION SETS

The chemical agents, which include sulfur mustard agents (HD and H), L, and the nitrogen mustards (HN-1 and HN-3), shown in Figures 1 and 1a, may not be transferred from the RRS to approved hazardous waste TSDFs without chemical treatment. They must first be converted to less toxic materials to allow release from Army control. Their structural formulas and chemical properties follow.

All of the chemical agents to be treated in the RRS are liquids although some of them are absorbed on charcoal. They are expected to range in purity from 80 to 95 percent. Little is known about the impurities that may be found in the CAIS items. Tables 4-1and 4-4 of this application provide some information on the impurities and degradation products of chemical agents based on munitions stockpile data and bench scale reactions. These chemical agents exhibit low solubility in water, and react with alkali hypochlorites, other oxidants, or alkalis in water or alcohols.

$Cl—CH_2—CH_2—S—CH_2—CH_2—Cl$

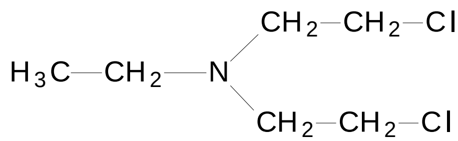


Sulfur Mustard, HD (H and HS are similar)
MW: 159.08.
Oily, amber to colorless liquid (b.p. 442°F + , 228°C + *; decomposes).
Odor: like garlic or horseradish.
Vapor pressure: low (0.09 mm at 86°F).
Density: 1.27 g/mL; 10.6 lb/gal.
Freezing point: 58°F, 14.5°C*.
Slightly soluble in water (0.9 parts/100 parts, by weight at 68°F).
Soluble in organic solvents such as chloroform, acetone, gasoline.
Reacts with oxidizing agents (peroxide, hypochlorite salts) to form sulfoxides and/or sulfones; reacts with alkali, ammonia, or amines to form substitution products.

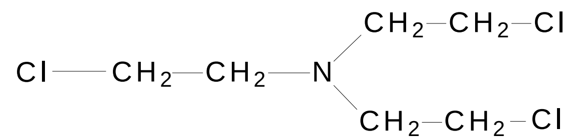
[* Some sulfur mustard materiel such as H may have lower freezing points and higher boiling points than those listed above.]

Lewisite, L
MW: 207.32.
Colorless to brown liquid (b.p. 374°F - decomposes, 190°C - decomposes).
Odor: like geraniums.
Vapor pressure: low (0.4 mm at 68°F)
Density: 1.89 g/mL; 15.8 lb/gal
Freezing point: -0.2 to 9°F, -18 to -13°C.
Insoluble in water and aqueous acids
Soluble in organic solvents, such as chloroform or acetone
Oxidizing agents (peroxide, hypochlorite salts) converts L to arsenic oxide derivatives; reacts with alkalis in water or alcohol.

Figure 1. Chemical and Physical Properties of Chemical Agents Found in CAIS



<u>Nitrogen mustard, HN-1</u>
MW: 170.08.
Oily, colorless to pale yellow liquid (b.p. decomposes on heating, rapidly above 200ºF).
Odor: faint fishy or amine.
Vapor pressure: 0.24 mm at 77ºF.
Density: 1.09 g/mL; 9.1 lb/gal.
Freezing point: -29ºF, -34ºC.
Sparingly soluble in water.
Freely soluble in acetone, chloroform and other organic solvents.
Forms a water soluble salt with acids; con-verted by oxidizing agents (peroxides or hypochlorites) to an amine oxide and other products.



<u>Nitrogen mustard, HN-3</u>
MW: 204.53.
Oily liquid (b.p. decomposes on heating, rapidly above 200ºF).
Odor: faint fish plus soap.
Vapor pressure: 0.011 mm at 77ºF.
Density: 1.24 g/mL; 10.3 lb/gal.
Freezing point: 25ºF, -3.7ºC.
Nearly insoluble in water.
Soluble in chloroform, acetone, and other organic solvents.
Forms water soluble salts with acids; reacts with oxidizing agents (peroxides or hypochlorites) to form an amine oxide and other products.

Figure 1a. Chemical and Physical Properties of Chemical Agents Found in CAIS

CHEMICAL PROPERTIES OF CHEMICAL TREATMENT REAGENTS AND SOLVENTS

A chemical treatment reagent is used to convert the chemical agents to less toxic products. The selection of a treatment reagent is complicated by the various criteria it must meet. A rapid and complete reaction is desired to allow a sufficient number of CAIS ampules or bottles to be processed through the RRS in a "reasonable" amount of time. Therefore, the rate of reaction has to be relatively fast at ambient temperature. A reaction is considered fast when the agent is 50-percent converted in less than 1 minute ($t_{1/2} < 1$ minute). The ratio of treatment reagent volume to the volume of CAIS materiel must be low to minimize the amount of waste generated. Minimums are depicted in Table 1. The quantity of heat generated from the reaction must be small to prevent excessive temperatures that could lead to undesirable decomposition of the treatment reagent. Also, the pressure generated in the closed reactor by the process should be negligible to prevent breakage of the rupture disk that would release the reaction components into the glovebox. The neutralent (residue from the chemical treatment reactions) formed in the reaction is suitable for analysis by documented analytical techniques, and that may be further managed at an approved hazardous waste TSDF.

The 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) dissolved in a solvent mixture of chloroform/t-butyl alcohol/water (solvent mix) will be used to chemically treat sulfur (HD and H) and nitrogen mustards (HN-1) and L in chloroform (K951/K952 and K953/K954 CAIS) and neat HD and H (K941/K942 CAIS). The solvent mix consists of 48.5 parts chloroform, 48.5 parts t-butyl alcohol, and 3 parts water, by volume. Figure 2 shows the physical and chemical properties of the reagent and solvents for this treatment process. The same DCDMH solution is used to treat L adsorbed on charcoal (in Navy training sets K955 and X548). The HD and H, HN-1 and HN-3 charcoal on CAIS items (in Navy training sets, K955, X302, X547, X550, and X551 CAIS) will be treated with DCDMH in chloroform. Figure 2a shows the physical and chemical properties of the reagent and solvent for this treatment process. The dissolved DCDMH provides 2 equivalents of free chlorine for each mole of DCDMH. Each chlorine equivalent oxidizes and/or chlorinates the agent, reducing its agent properties. Table 1 lists the grams of agent and DCDMH used for each process, the mole ratio of DCDMH to agent (moles DCDMH/moles agent) (assuming 100 percent DCDMH), and the chlorine equivalent for each mole of agent.

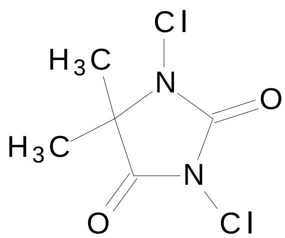
Table 1. Minimum Ratio of Reagent to Agent for each RRS Process

Process/Agent	DCDMH (gm)	Agent (nearest gm)	Moles DCDMH / Moles Agent (nearest 0.1 mole)	Cl Equivalent / Moles Agent
RED				
Sulfur Mustard	52.5	15	2.8	5.6
Lewisite	52.5	23	2.5	5.0
Nitrogen Mustard	52.5	13	3.5	7.0
BLUE				
Neat Sulfur Mustard	219	140	1.2	2.5
CHARCOAL				
Sulfur Mustard	174	32	4.4	8.8
Nitrogen Mustard	174	27	5.5	11.0
CHARCOAL-L				
Lewisite	96	47	2.1	4.2

Note:

Agent quantities listed are the maximum amounts of agent expected. For instance, agent dissolved in chloroform is nominally a 5 percent solution in chloroform, with observed values ranging from 3 to 10 percent by volume. Therefore, 10 percent by volume was the value used to estimate the maximum agent amounts in the calculations for this table.

Reagent

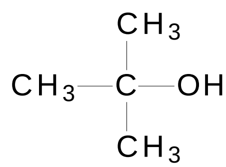


<u>1,3-Dichloro-5,5-dimethylhydantoin (DCDMH)</u>
MW: 197.02.
Fine, white powder.
Odor: Very slight pungent.
Melting point: 273-277ºF, 134-136ºC.
Slightly soluble in water (0.15 parts per 100 parts of water by weight at 77ºF).
Soluble in certain chlorinated solvents (14 parts per 100 parts of chloroform by weight) and aromatic solvents (for example, benzene or toluene), reacts with alcohols.
Reacts with readily oxidizable organics to form oxidation or chlorination products; decomposes and conflagrates when heated to 414ºF.

Solvent Mixture

$CHCl_3$

<u>Chloroform</u>(48.5 parts by volume)
MW: 119.38.
Colorless, mobile liquid (b.p. 143ºF, 62ºC).
Odor: sweetish, penetrating.
Vapor pressure: 159 mm at 68ºF.
Density: 1.48 g/mL; 12.3 lb/gal.
Freezing point: -82ºF, -63ºC.
Slightly soluble in water (0.8 parts/100 parts water by weight).
Miscible with most organic solvents.
Reacts slowly with air, in light, to form phosgene and hydrogen chloride (therefore, 0.7-1% ethyl alcohol or 40-100 ppm of amylene is added as stabilizer); reacts with strong alkali (sodium hydroxide); reacts with amines.



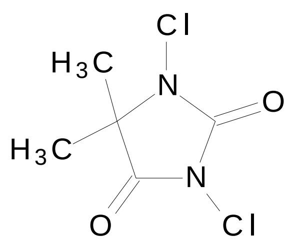
<u>t-Butyl alcohol</u> (48.5 parts by volume)
MW: 74.12.
Colorless liquid (b.p. 180ºF, 82ºC).
Odor: vaguely like camphor.
Vapor pressure: 44 mm at 79ºF.
Density: 0.781 g/mL; 6.52 lb/gal.
Melting point: 78.3ºF, 25.7ºC.
Miscible with water.
Soluble in most organic solvents.
Reacts with concentrated sulfuric acid or hydrochloric acids.

H_2O

<u>Water</u> (3 parts per volume)
MW: 18.016.
Colorless liquid (b. p. 212°F, 100°F)
Vapor Pressure: 23.8 mm at 77 °F.
Density: 0.997 g/mL; 8.32 lb/gal.

Figure 2. DCDMH Treatment Reagent for Sulfur, Nitrogen Mustard, Lewisite in Chloroform, Neat Sulfur Mustard, and Lewisite on Charcoal

Reagent



1,3-Dichloro-5,5-dimethylhydantoin (DCDMH)
MW: 197.02.
Fine, white powder.
Odor: Very slight pungent.
Melting point: 273-277ºF, 134-136ºC.
Slightly soluble in water (0.15 parts per 100 parts of water by weight at 77ºF).
Soluble in certain chlorinated solvents (14 parts per 100 parts of chloroform by weight) and aromatic solvents (for example, benzene or toluene), reacts with alcohols.
Reacts with readily oxidizable organics to form oxidation or chlorination products; decomposes and conflagrates when heated to 414ºF.

Solvent

$CHCl_3$

Chloroform Solvent
MW: 119.38.
Colorless, mobile liquid (b.p. 143ºF, 62ºC).
Odor: sweetish, penetrating.
Vapor pressure: 159 mm at 68ºF.
Density: 1.48 g/mL; 12.3 lb/gal.
Freezing point: -82ºF, -63ºC.
Slightly soluble in water (0.8 parts/100 parts water by weight).
Miscible with most organic solvents.
Reacts slowly with air, in light, to form phosgene and hydrogen chloride (therefore, 0.7-1% ethyl alcohol or 40-100 ppm of amylene is added as stabilizer); reacts with strong alkali (sodium hydroxide); reacts with amines.

Figure 2a. DCDMH Treatment Reagent for Sulfur and Nitrogen Mustards on Charcoal

TREATMENT REACTIONS

A CAIS ampule(s) or bottle and the appropriate amount of treatment reagent and solvent mix are added to the reactor. The reactor is sealed, the CAIS ampule(s) or bottle is then broken and the reactor contents are agitated intermittantly for a period of 15 minutes, as described in Attachment 2.

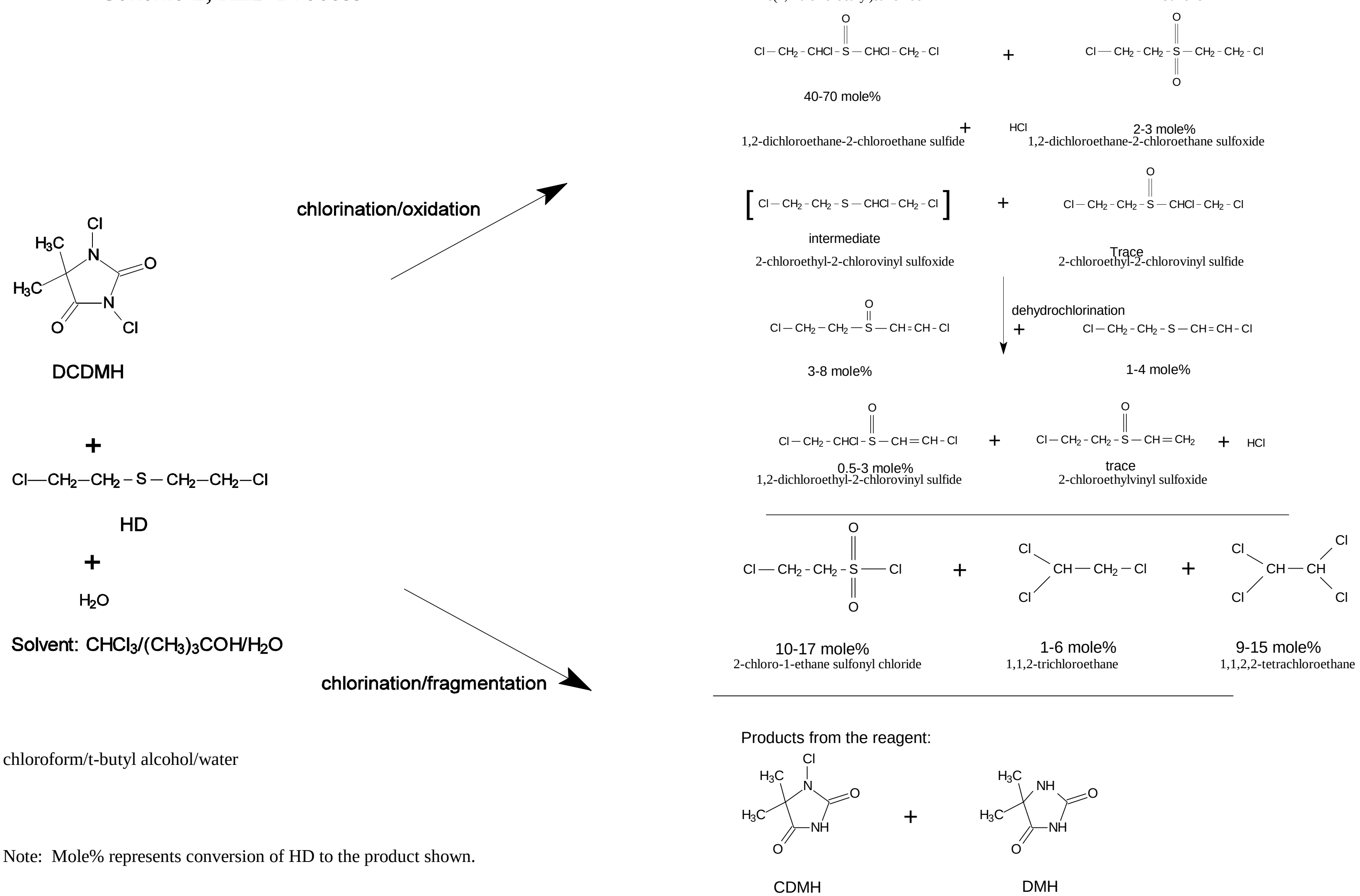
In the reagent solution DCDMH is not stable indefinitely. Therefore, the solution is prepared just before the reaction, as follows. After the CAIS item(s) is placed in the reactor, powdered solid DCDMH will be added to the reactor. Then the required volume of the solvent mixture will be added, the reactor will be promptly sealed, and ampules or bottle will be broken and the mixture will be agitated. Since the solid DCDMH is highly soluble in the solvent mix, it dissolves rapidly to allow its rapid reaction with the agents. In all of these processes, an excess of the treatment reagent is used to ensure complete reaction of the chemical agent.

RED Process. For the solutions of sulfur mustards (HD and H), nitrogen mustard (HN-1), or L in chloroform (all from K951-K954 CAIS), 18 g of DCDMH in 150 mL of solvent mix (Table 1) is used per CAIS ampule. This procedure is called the RED Process.

The reactions of the sulfur mustard that occur with DCDMH in the presence of water are shown in Scheme 1. In this process, DCDMH reacts with the HD to form several products. These products result, in a major part, from a simple chlorination and, with the participation of the water in the solvent, from an oxidation of the organic sulfides to chlorinated sulfoxides and sulfones. A loss of hydrogen chloride (HCl) from the initial products leads to the formation of chlorovinyl chloroethyl sulfoxides and a small amount of 2-chlorovinyl 2-chloroethyl sulfide. At the same time, the reagent also causes some of the carbon sulfur bonds of the HD to be cleaved to form a mixture of 2-chloroethylsulfonyl chloride and tri- and tetrachlorinated ethanes. The DCDMH is consumed by dechlorination first to form chlorodimethylhydantoin (CDMH) and then to form dimethylhydantoin (DMH). The mole percent values shown in Scheme 1 represent the conversions of HD to products that have been observed in laboratory studies. The products from this reaction are all soluble in the solvent mixture.

L is chemically converted to a single product by DCDMH, chlorovinylarsonic acid (CVAOA), as shown in Scheme 2. The reaction requires the water in the solvent to both hydrolyze the chlorines on the arsenic to hydroxyl groups and to participate in the oxidation of the arsenic. The CVAOA is soluble in the solvent mix.

Scheme 1, RED Process



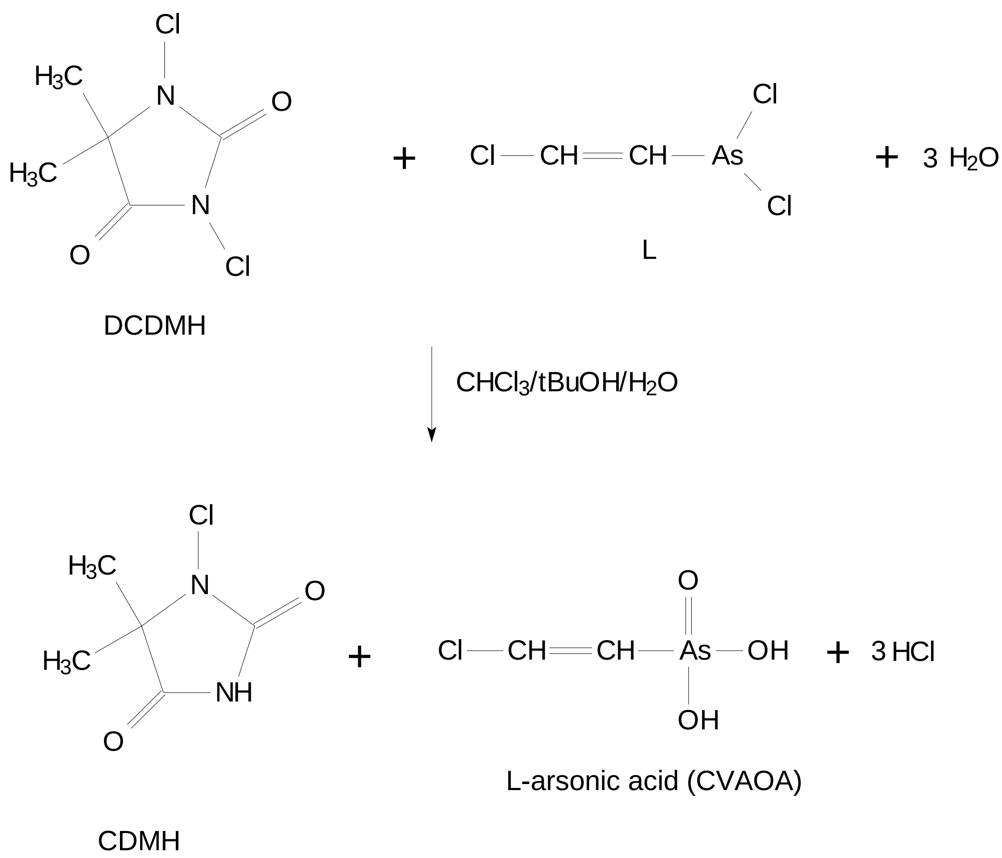
chloroform/t-butyl alcohol/water

Note: Mole% represents conversion of HD to the product shown.

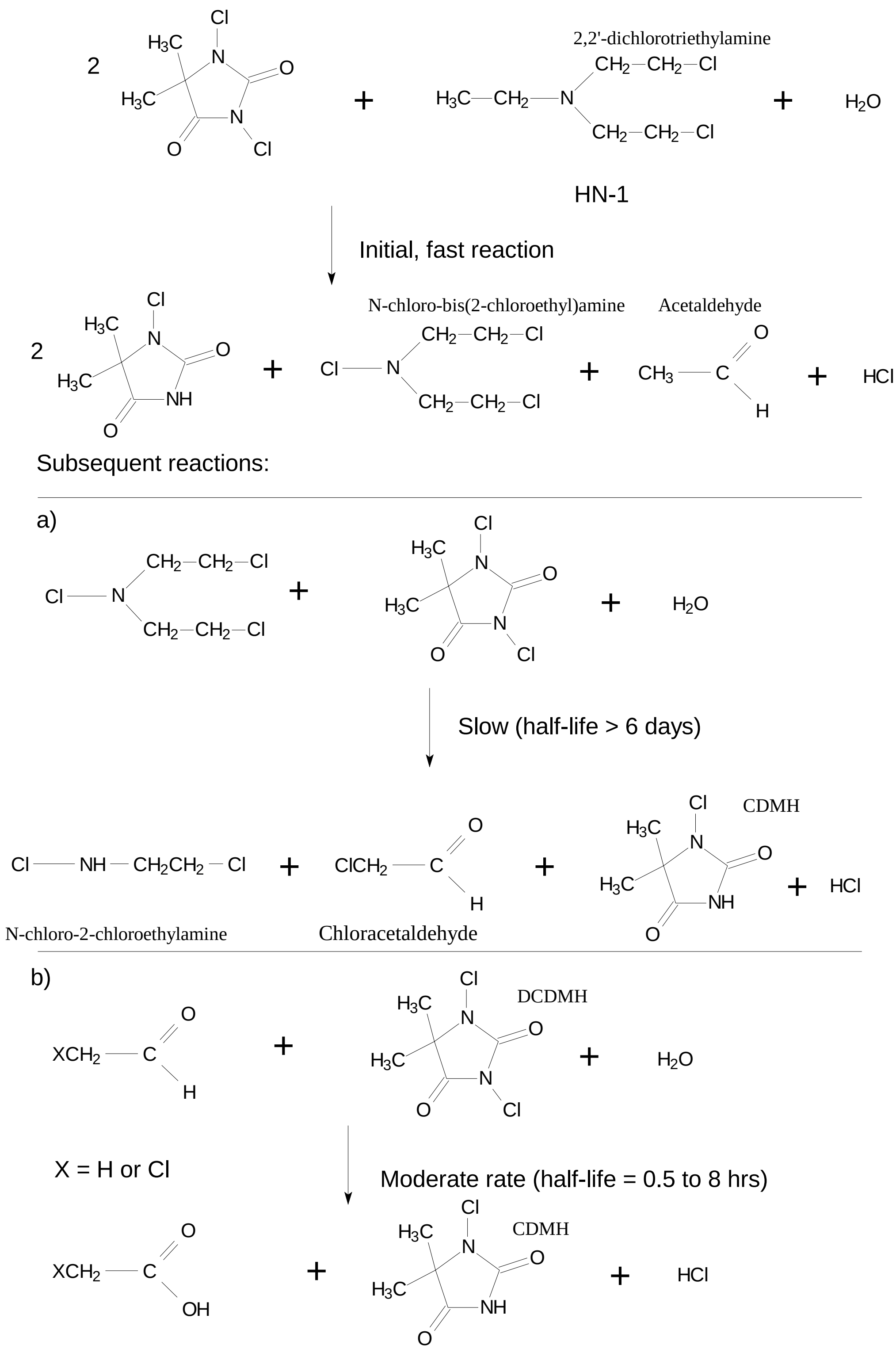
The reaction of the nitrogen mustard (HN-1) is shown in Scheme 3. The reaction process is a series of cleavages of the nitrogen to carbon bonds and oxidations. The first step of the process is the immediate cleavage of the ethyl group to yield N-chlorobis(2-chloroethyl)amine and acetaldehyde. Because excess DCDMH or CDMH is used, a chloroethyl group of the N-chloro-bis(2-chloroethyl)amine is slowly cleaved and oxidized producing chloroacetaldehyde and N-chloro-2-chloroethylamine. The acetaldehyde and chloroacetaldehyde are both further slowly oxidized to form acetic acid and chloroacetic acid as shown in scheme 3b. The residual oxidizing material (DCDMH, CDMH, and various N-chloroamines) will slowly chlorinate the chemical agent products, the t-butyl alcohol, and the methyl groups on the hydantoins. All of the products are soluble in the solvent mix.

A yellow color is produced when HD or HN-1 is mixed with DCDMH solution. This color change is probably due to the release of chlorine, which is reduced to hydrogen chloride as the reaction proceeds. The L reaction with DCDMH produces a green color, possibly resulting from the change in oxidation state of the arsenic.

Scheme 2, Red Process, L Reactions



Scheme 3, Red Process, HN-1 Reactions

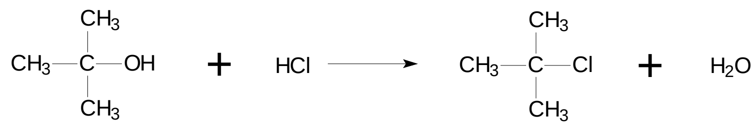


The rate of reaction between DCDMH and HD, HN-1, and L CAIS is fast, $t_{1/2} < 30$ seconds, at room temperature. Because of the relatively low concentrations, the heat generated by the reactions cause the mixture to increase in temperature by only a few degrees. When the process is run in a closed reactor, a maximum of 5 pounds per square inch gauge (psig) pressure has been observed. To ensure that all of the reagent and solutions from the broken ampules are completely mixed, and to confirm that the chemical agent concentrations are below the limits described in Table 4-5, the treatment process mixtures are agitated for 15 minutes. Analysis of the waste indicates that the concentration of residual chemical agent is below 50 mg/L following the 15-minute contact time (contact time or agitation period refers to the amount of time DCDMH is in contact with the chemical agent in the reactor). Any trace amounts of the agents that remain after the reaction in the reactor will continue to be in contact with the DCDMH or CDMH in the waste drum.

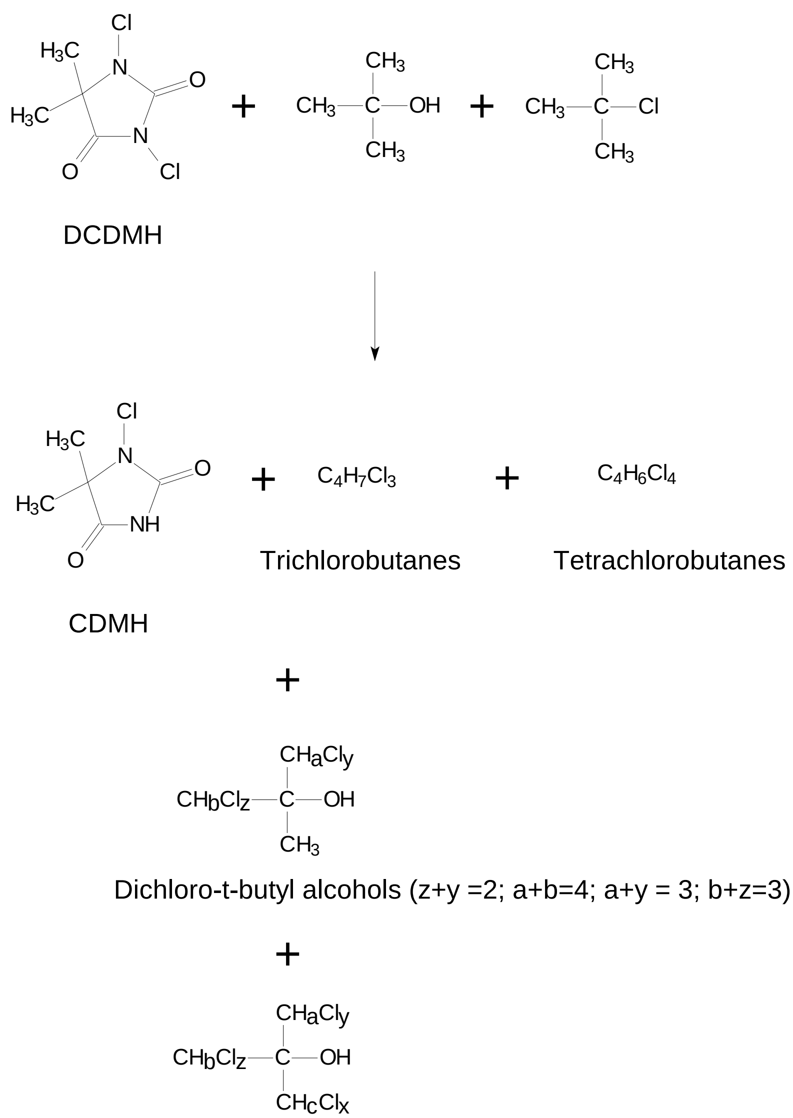
Other reactions occur which produce essentially non-toxic products; these merit identification because they may appear as major products following each reaction shown in Schemes 1-3. The hydrogen chloride, HCl, formed as shown in Schemes 1-3 can be expected to react with the t-butyl alcohol to form t-butyl chloride as shown in Scheme 4a. This well known process is expected in this solution. Trichloro- and tetrachlorobutanes were found in the solution; further chlorination of the t-butyl chloride may have consumed all of this intermediate. Excess DCDMH and/or CDMH is present after completion of the 15-minute period of agitation as confirmed by iodometric titration for available chlorine or by Nuclear Magnetic Resonance (NMR) analysis for CDMH and/or DCDMH. With time the excess available chlorine will chlorinate the reaction products, including chemical agent products, t-butyl alcohol, and dimethylhydantoin, until exhausted. However, these chlorinations are very slow. The t-butyl alcohol cosolvent will react with excess available chlorine from the DCDMH or CDMH to produce a series of chlorinated butanes and butenes and chlorinated t-butyl alcohol, including: trichlorobutanes, tetrachlorobutanes, tetrachlorobutenes, and dichloro- and trichloro-t-butyl alcohols, as shown in Scheme 4b.

Scheme 4, Chlorobutanes Formation

a)



b)

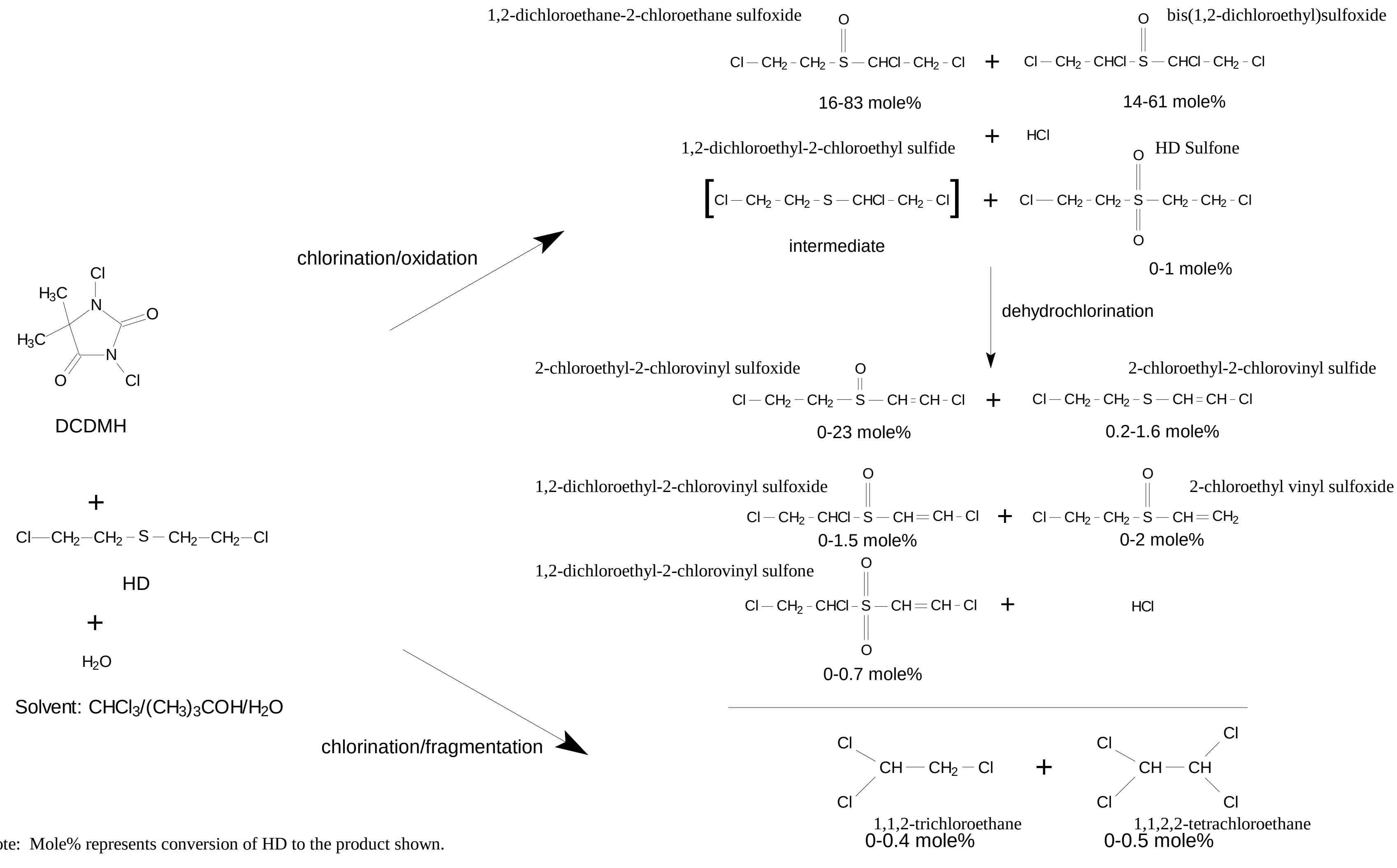


Trichloro-t-butyl alcohols (z+y+x =3; a+b+c=6; a+y = 3; b+z=3;c+x=3)

BLUE Process. For the K941 and K942 CAIS, which contain neat HD or H, 219 g of DCDMH and 2,068 mL of solvent mix (see Table 1), is used per CAIS bottle. This procedure, called the BLUE Process, is shown in Scheme 5. The reaction is similar to the RED process reaction that converts HD to products (see Scheme 1), but the relative amounts of compounds formed are different. The major portion of the products, 2-chloroethyl dichloroethyl sulfoxides and bis-(dichloroethyl) sulfoxides, are formed in the chlorination/oxidation step along with small amounts of the HD-sulfone [bis-(2-chloroethyl) sulfone]. Various quantities of chlorinated ethyl vinyl sulfoxides, 2-chloroethyl 2-chlorovinyl sulfide, and a small amount of 2-chloroethyl 2-chlorovinyl sulfone have been observed in the laboratory tests of this HD treatment method. Trace amounts of trichloroethane and tetrachloroethane were also found; see Scheme 5 for the ranges of products that are expected in the treatment process. Although the DCDMH reagent is also used in this BLUE process, the product mixture is somewhat different from that in the RED process, because HD is present in higher concentration and no other agent is present.

The rate of reaction is very rapid, $t_{1/2} < 30$ seconds at room temperature, and a negligible amount of pressure is generated. Heat is evolved in the process, but the solution temperature was observed to rise by less than 40^{o}C. Excess DCDMH or CDMH is present after completion of the treatment reaction. The excess reagent was confirmed by an iodometric titration for available chlorine, and by an NMR analysis for residual DCDMH or CDMH. With time, the excess available chlorine will chlorinate the HD reaction products, t-butyl alcohol, and the methyl groups of the dimethylhydantoin, until exhausted. Chlorobutanes are slowly formed from the t-butyl alcohol as shown in Scheme 4; no chlorinated t-butyl alcohol was found in the BLUE product mixture. The concentration of residual sulfur mustard following a contact time of 30 minutes is below 50 mg/L.

Scheme 5, BLUE Process



Note: Mole% represents conversion of HD to the product shown.

Products from the reagent: CDMH + DMH

CHARCOAL Process. Two methods are used to treat agents-on-charcoal with DCDMH. For the sulfur mustards (HD or H), or the nitrogen mustards (HN-1 and HN-3) adsorbed on charcoal (K955, X302, X547, X548, X550, and X551 CAIS) chloroform is used as a solvent (174g of DCDMH in 967 mL of chloroform per bottle, see Table 1). For L adsorbed on charcoal the mixed chloroform/t-butyl alcohol/water solvent is used (96g of DCDMH in 824mL solvent per bottle, see Table 1). These procedures are designated as the Charcoal Process and Charcoal "L" Process, respectively. The solvent mix, for L treatment, is the same as that used in the RED process, and the products formed are the same. The treatment of the sulfur mustards (HD or H), nitrogen mustards (HN-1 and HN-3) with DCDMH in chloroform solution causes the formation of different products than those that are formed in the RED process. The product mixtures from the H and N mustards are mixed with the product mixture from the L on charcoal in the waste drum. The admixture of the water in the components of the "L" Charcoal Process solvent with the H and N mustard products allows additional reactions to occur.

The chemical agents on the charcoal are distributed in the porous structure of the charcoal. This preparation immobilized the liquid chemical agents to allow their use for training troops to recognize the odors of the agents. The charcoal contains pores of various sizes, which are defined as micropores (<20 Å), mesopores (20-500 Å), and macropores (>500 Å); as much as 10 percent of the chemical agent is adsorbed in the micropores. Before a chemical treatment reaction can occur, reagent and chemical agent must make contact. Therefore, either the chemical agent must diffuse out of the small pores, or the DCDMH must penetrate into the smallest pores. Chloroform rapidly penetrates the macro-, meso-, and micropores to assist the dissolution and diffusion of the reactants, in and out of the pores. The DCDMH reacts with the chemical agents either by migrating into the pores, along with the solvent, or reacting with the chemical agent as it fluxes from the pores. The DCDMH in solution has been found to penetrate the smallest of charcoal pores and selectively react with the chemical agent, while leaving the charcoal unreacted. This result is desirable, unlike some other candidate treatment reagents for chemical agents that were found to also react with the charcoal.

To determine the efficiency for each of the reactions between DCDMH and the chemical agents, adsorbed on the charcoal, both the liquid layer (solvent) and solid layer (charcoal) were analyzed after the treatment was complete. For these reaction studies agents-on-charcoal were prepared in the laboratory by pouring the required amount of chemical agent onto previously-dried granulated charcoal contained in a glass jar. The jar was then sealed and mixing was accomplished by tumbling of the jar contents by rotating the jar on rollers for 2 hours. The mixture was then stored for at least 24 hours to allow the adsorbed material to reach an equilibrium distribution on the charcoal. The loading of agent on the charcoal was 25 mL agent/90 mL charcoal, equivalent to the concentration used in the CAIS bottles. To determine the amount of chemical agent remaining on the charcoal after the DCDMH treatment, the separated solid was continuously extracted with chloroform for 12 to 18 hours in a Soxhlet extraction apparatus. The extract was then evaporated to dryness at 40^0C in a stream of argon, and the residue was then reconstituted in 1 mL of chloroform. The Soxhlet extract and the product solutions were then analyzed for the respective chemical agents.

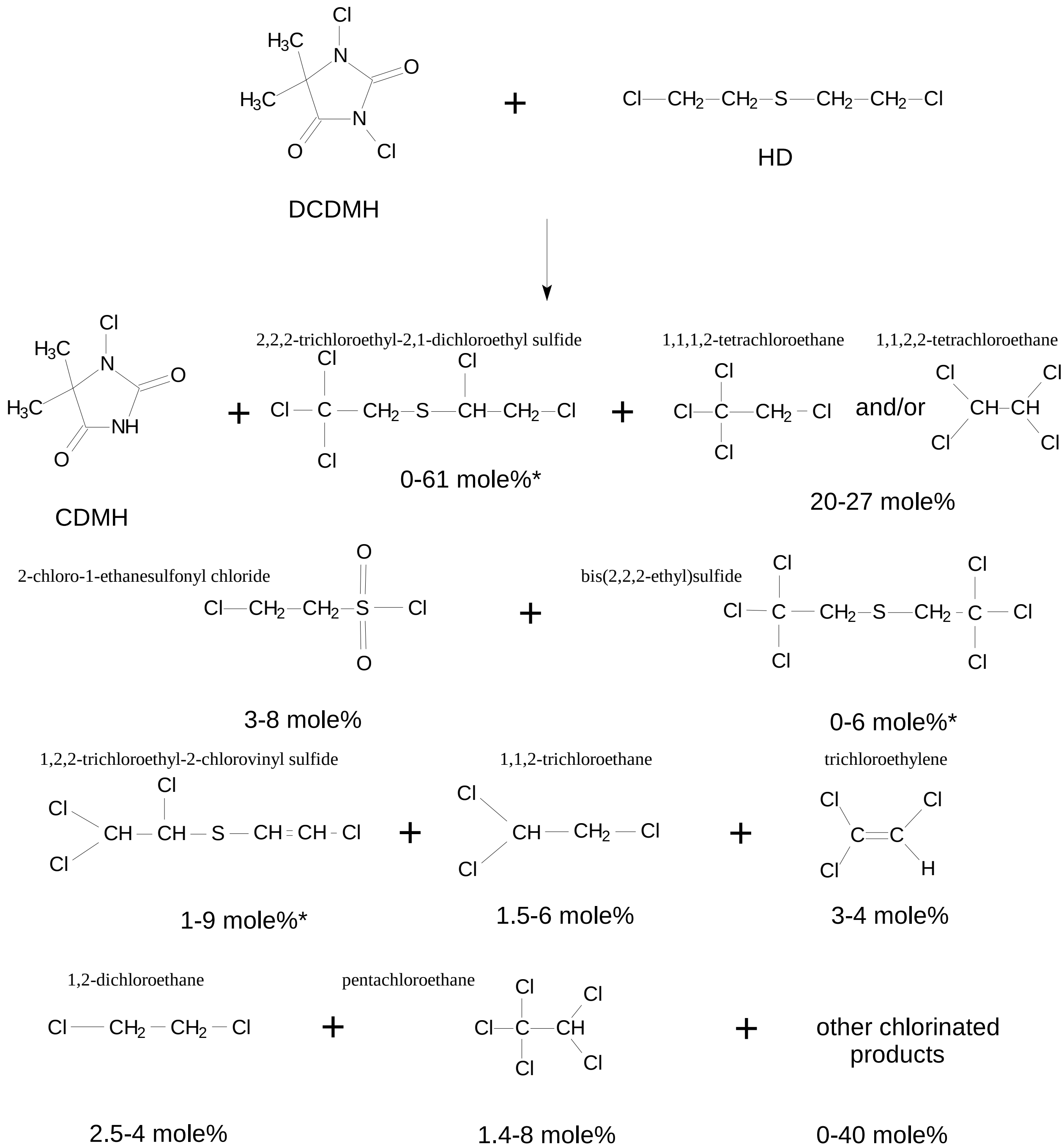
Scheme 6 illustrates the reaction between DCDMH and HD adsorbed on charcoal as developed from gas chromatograph/mass spectrometer analyses of the solution and the Soxhlet extract from the charcoal. The analyses of the solution indicated that HD was reduced to less than 50 mg/L within

15 minutes, but the conversion of all of the HD adsorbed in the charcoal required longer. The HD in the Soxhlet extract from the charcoal did not decrease below the quantitation limit of 50 mg/L until the process was continued for 30 minutes. A large excess of DCDMH is used in this reaction and a variety of chlorinated products are produced. Chlorinated sulfides, polychlorinated ethanes, and polychlorinated ethylenes appear as major products. Since no water was added in these laboratory studies, no significant amounts of oxygen-containing products are formed. Thus, the process is different from the RED process. The mono-substituted chlorodimethyl-hydantoin and the dimethylhydantoin appear as major products from the treatment reagent. The distribution of these products could vary greatly depending on the amount of initial chemical agent. Hexachloroethane, trichloroethylene, and sulfur dioxide have been identified as minor products; several minor products were detected chromatographically, but not identified. The small quantity of 2-chloroethylsulfonyl chloride formed in some experiments probably resulted from the presence of a trace amount of water in the reactor.

The reaction of DCDMH with HN-1 on charcoal is shown in Scheme 7. Based on the analyses of the products, it is concluded that the DCDMH primarily chlorinates the ethyl group of the HN-1, along with some chlorination of the 2-chloroethyl groups. Apparently the carbon-nitrogen bond of the agent is cleaved, along with the chlorination to form chloroethanes (or chloroethylenes) which are further chlorinated to form dichloroethanes. Chloral was observed as one of the products; this is assumed to result from traces of water that may have entered the reaction mixture as an impurity. The formation of chlorovinyl amine derivatives, as shown in Scheme 7, probably results from the loss of hydrogen chloride from polychlorinated amines. This reaction is also completed within 30 minutes. The reaction of DCDMH, in the mixed solvent, with L on charcoal produces one product, CVAOA. This process is nearly identical to the reaction that occurs in the RED process, as shown in Scheme 2. In the presence if the charcoal, a small amount of tetrachloroethane is also formed. The reaction is fast, as discussed below.

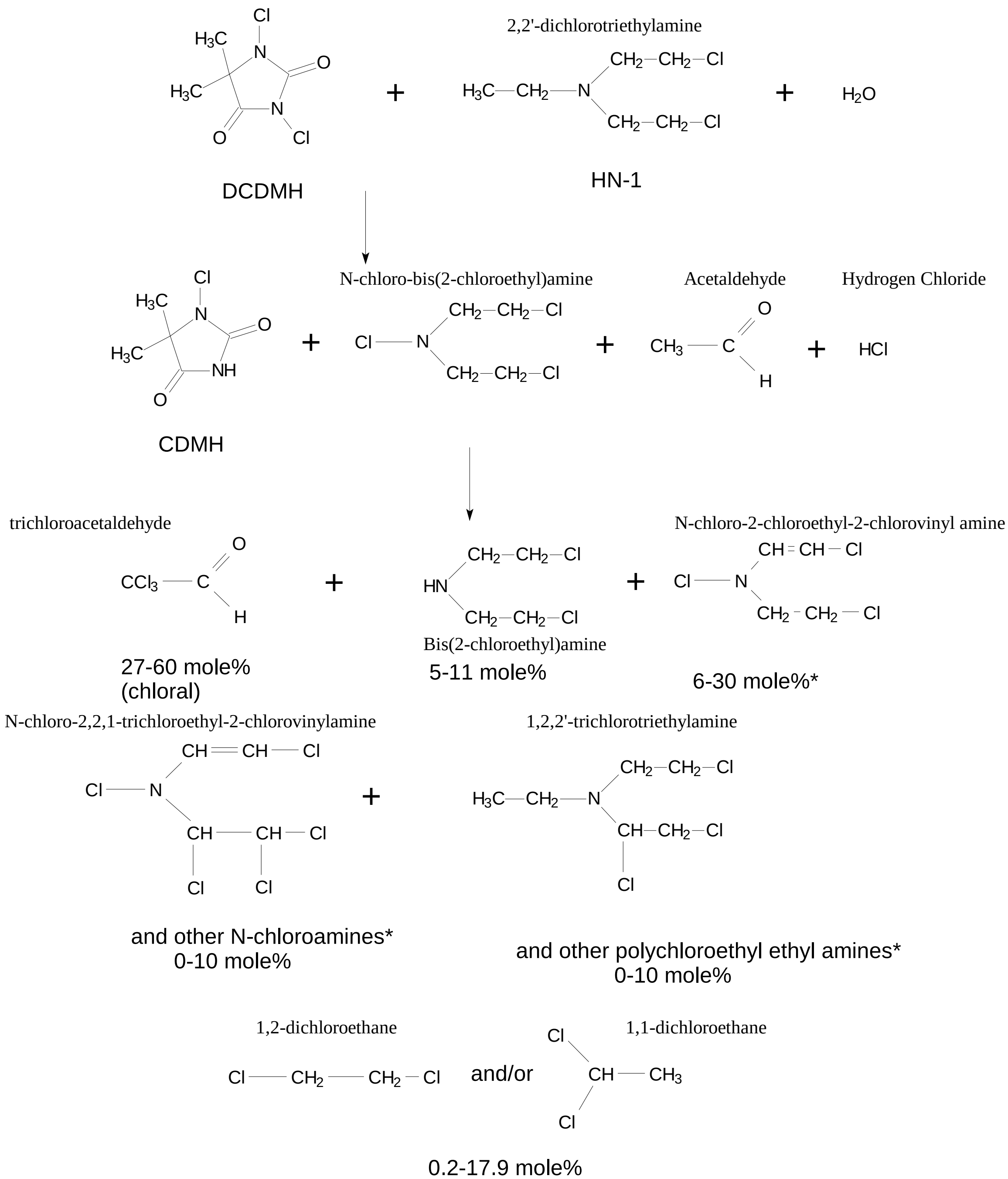
The rate of reaction between HD, HN-1, and L and DCDMH in the liquid layer is too fast to measure by removing samples and analyzing them periodically. The rate of the reaction in the charcoal pores also could not be measured. The concentrations of chemical agents (HD, HN-1, and L) in the liquid layer were found to be below 50 mg/L, the quantitation limit, following a 15 minute contact time. The concentrations of chemical agent in the charcoal Soxhlet extracts were below 50 mg/L after a 30-minute contact time, but measurable levels of agent were present earlier. Therefore, these results show that after 15 minutes, the agent remaining in the charcoal is still reacting with the DCDMH. A slightly increasing reaction temperature beyond the 15-minute period also indicates that the reaction is not complete. The Army expects that the agent concentration is less than the level of quantification after 30 minutes; however, the reaction will continue in the waste drum. The pressure and temperature observed in the laboratory for these reactions did not exceed 2.5 psig and 35^0C, respectively. These levels are well below the limits allowed by the reactor design. Excess concentrations of DCDMH and CDMH, have been found to be present up to 36 hours in the mixture. This insures that the chemical agent treatment will be complete in the waste drum. The presence of available chlorine, from the DCDMH and CDMH, can easily be detected with starch-iodide indicator paper.

Scheme 6
CHARCOAL Process, HD Reactions



*Isomeric mixtures, only one isomer is shown.

Scheme 7
Charcoal Process, HN-1 Reactions



Mole% represents conversion of agent to product.
*Isomeric mixtures, only one isomer is shown.

In the test of the RRS various types of agents on charcoal will be treated if those types of CAIS items are found at DCD. The present data does not indicate the types of agent (sulfur mustard, nitrogen mustard, or L) in the inventory of items to be treated. The treatment residue from any of the agent-on-charcoal bottles will be combined in the waste drum. If no L is treated in the test, the products of the charcoal process will be as described in Schemes 6 and 7, but if L is treated further reactions will occur as shown in Scheme 8. These reactions occur because water is introduced into the mixture, and water allows the oxidation of the sulfur mustard products to sulfoxides and sulfones and oxidation of the nitrogen mustards to chloral hydrate and bis-(2-chloroethyl)amine. Because t-butyl alcohol is also introduced, various chlorobutanes are also formed, as observed in the RED process (see Scheme 4).

Scheme 8

Reactions in the Combined Waste from the Charcoal Processes

"C-L": DCDMH + lewisite in $CHCl_3$/tBuOH/H_2O